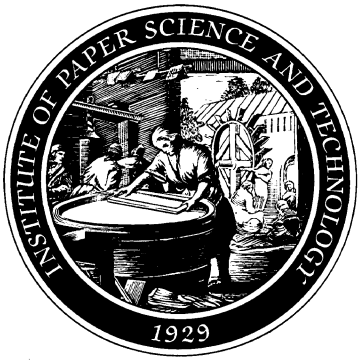


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# Determination of VOC Contents in Kraft-Mill Streams Using Headspace Gas Chromatography

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## ABSTRACT

The emission of volatile organic compounds (VOC's) in pulp and paper mills has been an environmental concern in many countries. VOC content in mill streams is one of the key factors dictateing VOC emissions. Unfortunately, few methods are available to quantify the VOC liquid content in various mill streams because of the corrosive nature of most mill streams, such as black liquor, which prevents direct composition analysis using traditional analytical methods, for example, direct injection into gas chromatography (GC). This paper reports a new method for the measurements of VOC liquid content in mill streams based on vapor liquid phase equilibrium of the species to be measured using a commercial headspace GC system. Experimental data showed excellent agreements between the quantity measured and the amount known in various types of standard VOC-water mixture solutions. The liquid methanol contents measured in four black liquor samples using the present method also agree with our previous study using the method developed by NCASI. The present method is rapid, accurate, and automated.

***Keywords***: VOC; Henry's law; headspace; GC; standard addition; black liquor; mill streams.

## INTRODUCTION

With the increasingly restrictive environmental regulations, maintaining environmentally sound and technologically competitive operations in pulp and paper mills is a key to the success of the pulp and paper industry. In the United States of America, the new toxic and permit provisions of the 1990 amendments require information on emissions of volatile organic compounds (VOC's) from pulp and paper mill sources. Many VOC's are now considered hazardous air pollutants (HAP's). The release of VOC's during mill operations is determined by several factors: (1) the VOC content in mill streams, (2) the fundamental thermodynamic phase equilibrium behavior of the VOC's in mill streams, (3) convection mass transfer associated with specific mill processes, and (4) the mill operating conditions, such as wood species, pulping chemicals used, water reuse in operation, etc. Therefore, the quantification of VOC content in kraft mill streams is very important for the understanding of VOC emissions and emission predictions using computer simulation models.

Several studies on VOC emissions at Kraft mills have been conducted. Venketesh et al. [1] reported a millwide VOC prediction using the process simulation technique. The American National Council of the Paper Industry for Air and Stream Improvement (NCASI) conducted a series of studies on VOC emission at Kraft mills. NCASI's study indicated that [2]: (1) the brownstock drum washer system, oxygen delinginfication system, smelt dissolving tank, bleach plant, and unbleached paper machine are the major contributors to VOC emissions from Kraft mills; (2) methanol constituted the major fraction of VOC emission from all sources; and (3) water reuse practice will significantly contribute to VOC emission in Kraft mills.

Unfortunately, the quantification of VOC content in mill streams from the above- mentioned systems is difficult. Limited measurement techniques are available due to the corrosive nature of those mill streams such as weak black liquor from drum washer systems, green liquor from smelt dissolving tanks, etc. In a previous study, we reported the measurement of liquid methanol content in weak black liquors using the method developed by NCASI [3]; however, the method requires the addition of chemicals to precipitate the solids in weak black liquors. The method has several disadvantages: (1) the amount of chemicals added (mass ratio of chemical over black liquor = 30:1) significantly dilutes the VOC concentration in the sample and reduces the measurement accuracy. It also prevents the measurement of low concentration VOC's in the sample, such as methyl ethyl ketone (MEK), etc.; (2) the method is only suitable for the analysis of weak black liquors as the solid precipitation method may not be used for other mill streams; and (3) the method is tedious, time consuming, and not applicable for on-line analysis.

The headspace gas chromatographic (HSGC) method [4] has been widely applied for identification of individual components and substance groups present in complex mixtures, as well as for physicochemical and vapor-liquid phase equilibrium (VLE) measurements [5]. Because headspace sampling relies on the volatilization of the species to be measured to separate the compounds from sample matrices, sample clean-up and preconcentration are not necessary, and tedious and error-producing steps can be eliminated. Thus, the volatile compounds in almost any matrix can be analyzed easily and quickly by headspace gas chromatography. Much research on vapor-liquid phase equilibrium has been conducted

using commercial headspace GC systems [6, 7]. Rapid and automated measurements can be carried out using commercial headspace GC systems.

We have developed an indirect measurement method for the quantification of VOC content in liquid samples by headspace gas chromatography. The method is based on the thermodynamic vapor-liquid phase equilibrium of the species to be measured. In this study, we applied the developed method to measure VOC concentration in the mixtures of VOC-water and in mill streams using a commercial headspace GC system.

## METHODOLOGY

According to Henry's law, the infinite small amount of solute dissolved in a liquid at equilibrium is proportional to the partial pressure of the gas, that is,

$$P_i = HC_i \qquad \text{or} \qquad H = \frac{P_i}{C_i}. \tag{1}$$

When a sample solution is introduced into a closed system with a headspace, a certain amount of solute will be transported from the liquid phase into the gas phase to become vapor through the liquid-gas interface, while a certain amount of vapor can diffuse into the solution at the interface. These two mass transport processes will reach a dynamic equilibrium after sometime. We call that the system reaches an equilibrium state between the vapor and liquid phase. The partial pressure of the solute in the vapor phase is proportional to the concentration of the solute in the liquid. The proportionality coefficient is the Henry's constant of the solution.

Under the vapor-liquid equilibrium state, the amount of solute in the vapor phase can be described as:

$$n_1 = C_0 V_l^0 - C_1 a V_l^0 = \frac{P_1 V_g^0}{RT}, \tag{2}$$

where we assume that the vapor phase solute in the headspace follows the ideal gas law.

If a certain volume of concentrated solution with a known concentration of the solute is added into this system, the existing equilibrium will be disturbed and a new equilibration state will be reached after a while. The amount of solute in the vapor phase under the new equilibration state can be expressed as:

$$n_2 = C_0 V_l^0 + C_s V_s - C_2 a V_l^0 = \frac{P_2 V_g^0}{RT}. \tag{3}$$

From Eqns. (2) and (3), we can obtain the concentrations of the solute in the liquid phase under the two equilibrium states,

$$C_1 = \frac{C_0 V_l^0 RT - P_1 V_g^0}{a V_l^0 RT}, \text{ and} \tag{4}$$

$$C_2 = \frac{C_0 V_l^0 RT + C_s V_s RT - P_2 V_g^0}{a V_l^0 RT}, \tag{5}$$

where we assume that the total volume of the solution remains the same as long as the volume of the concentrated solution added is negligible compared to the initial volume of the solution, i.e., $V_l^0 >> V_s$.

Under infinitive dilution, the Henry's constant is not dependent on the solute concentration in the solution. Therefore, we have

$$H = \frac{P_1}{C_1} = \frac{P_2}{C_2}. \tag{6}$$

Then, the initial solute concentration in the sample solution can be calculated from Eqns. (4) to (6) as,

$$C_0 = \frac{C_s V_s}{(P_2 / P_1 - 1)V_l^0}, \tag{7}$$

where the solute vapor partial pressure $P_1$ and $P_2$ in the vapor phase can be measured using an headspace GC. The reading from GC is the peak area of the species detected, which is proportional to the sample loop volume of the GC system and the solute partial pressure (solute concentration in the vapor phase), i.e.,

$$A_i = KV_{loop}P_i. \tag{8}$$

Substituting Eqn. (8) into Eqn. (7), we can find the concentration of the solute in the sample solution through headspace GC measurements,

$$C_0 = \frac{C_s V_s}{(A_2 / A_1 - 1)V_l^0}. \tag{9}$$

Eqn. (9) is the mathematical expression of the present method for measurements of liquid content of trace species in sample streams.

## EXPERIMENTAL

### Chemicals

Methanol, methyl ethyl ketone (MEK), and acetone are mixed with deionized water to make standard solutions of methanol-water, MEK-water, and acetone-water to validate the present method. The ranges of the concentration of these three standard solutions are 100-2000, 10-100, and 1-10 ppm, respectively, to match their liquid contents in typical Kraft mill streams. The combination of these three concentration ranges covers trace species concentrations over three orders of magnitude within the infinite dilution assumption limit.

Four pulping black liquor samples from two separate Kraft mills (Mill A and Mill B) were used for comparison studies of the measured liquid methanol content using the present method and the method developed by NCASI.

Measurements of liquid methanol contents were also conducted in various Kraft mill streams from Mill C.

### Apparatus and Operation

All measurements were carried out using an HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatography (Hewlett-Packard). Fig. 1 shows a schematic diagram of an HP Headspace Sampler. The operation of the sampler is very simple. A sample is first placed in a vial and sealed. The unfilled space in the vial is called the headspace of the sample. The sample is then transported to the headspace oven (a well-controlled temperature environment). The sample will undergo an equilibration period to

achieve vapor-liquid phase equilibrium. The sample vial is pressurized by helium for sampling purposes when valves S1 and S2 are open and the sampler's positions 5 and 6 are connected. The vapor phase in the headspace to be analyzed is filled in the sample loop when valves S1 and S2 are closed and the positions of 6 and 1 of the sampler are connected. The vapor in the sample loop is passed to the GC column by helium carry gas when the positions of 1 and 2, and 3 and 4 of the sampler are connected. The sample is equilibrated again in the sample loop. The entire operation described above is controlled by a personal computer.

GC conditions: HP-5 capillary column at 30°C; carrier gas helium flow (He): 3.8 mL/min. A flame ionization detector (FID) was employed with hydrogen and airflows of 35 and 400 mL/min, respectively. Headspace operating conditions: 25 minutes gentle shaking for equilibration of the sample, vial pressurization time 0.2 min, and sample loop fill time: 1.0 min., loop equilibration time: 0.05 min.

The sample preparation and measurement procedures were as follows: pipette duplicate 10 mL of sample solution into two 20-mL vials: add 10 μL of pure methanol solvent by microsyringe in one of the vials; then, close the vials and put into the headspace sampler for measurement.

## RESULTS AND DISCUSSIONS

### *The method of standard addition*

We applied the method of standard addition to develop a measurement technique for VOC content measurements in sample solutions in this study. The method of standard addition (or the known increment method) is widely used in many analytical approaches, such as potentiometry, polarography, and atomic spectroscopy [8]. In this method, a certain volume of solution with a known concentration of the solute is added into the sample solution (called "standard addition"). By measuring the signal changes before and after this "standard addition," the concentration of the solute in the sample can be calculated. The main advantage of this method is that it can measure analyte concentration in the samples having a high but unknown total ionic strength or for samples with highly variable solution components. Meanwhile, it does not require the preparation of a calibration curve.

### *Equilibration time*

When the sample solution is introduced into a closed system (vial) with a headspace, it needs a certain amount of time to reach an equilibrium state. The methanol concentration in the vapor phase is a function of time before it reaches the phase equilibrium state. The present method is based on the vapor-liquid phase equilibrium of the analyte under infinite dilution. Experiments were conducted to obtain the equilibrium state by measuring the vapor phase methanol concentration under varying equilibration time using the same sample. The results indicated that an equilibration time of 25 min is sufficient for the sample to reach equilibrium as shown in Fig. 2.

*The temperature of headspace sampler*

All experiments were conducted under the headspace sampler temperature of 70°C to avoid water vaporization and obtain a good sensitivity as sufficient methanol will be present in the vapor phase at this temperature. A temperature of 70°C is also close to the operating temperature of mill streams.

*Experimental technique validation*

The repeatability of the method was demonstrated by using a standard methanol-water solution (methanol = 800 ppm). A relative standard deviation (RSD) of measured liquid methanol content is less than 5.0% for the five solution samples tested, indicting that the repeatability of the technique is excellent.

The experimental technique is validated using a set of standard VOC-water (methanol-water, MEK-water, and acetone-water) solutions with known concentrations. The present method measures the VOC concentration of the standard solution according to Eqn. (9), where the GC peak areas $A_1$ and $A_2$ were obtained from the measurements of the vapor sample in the headspace taken before and after the standard addition of each solution. For a combined VOC concentration range of 1-2000 ppm described previously, the comparison between the standard and the measured data is excellent. A perfect correlation between the standard and the measured is shown in Fig. 3. The errors for all the measurements were less than 5.0%.

*Chromatographic peak separation of various compounds in black liquor vapor*

Many Kraft mill streams consist of various compounds, which will be present in their vapor phase. Accurate measurement of methanol vapor concentration in mill streams requires the elimination of interference from other substances on the chromatography. Black liquor is one of the most difficult mill streams for GC analysis as it contains many hydrocarbons and sulfur compounds. Fig. 4 shows a GC chromatogram of the vapor phase of a hardwood black liquor using a FID detector. The GC mass spectroscopy was used to identify the various compounds contained in the vapor phase as shown in the table in Fig.4. Through optimization, the major interference from α-pinene, β -pinene, and dimethyl sulfide can be eliminated under the GC conditions for the present study.

*Method comparison between determined methanol concentrations in mill black liquors*

Table I shows the methanol concentrations in different black liquors. It can be seen that the data obtained by the present method have a good agreement with the results obtained in the previous work [9] using the method developed by NCASI. The same conclusion can be made, that is, the methanol contents in the hardwood black liquors were higher than those in the softwood black liquors. The difference in measuring methanol contents between these two methods can mainly be attributed to the larger experimental error (about 10%) in NCASI's method in which a dilution factor of 30:1 was used in adding buffer solution to precipitate solids. Significant dilution of samples will always decrease precision in any analytical measurements.

It should also be pointed out that the measured liquid methanol concentration varies with the solid content of the streams as shown in Table I. In general, a high solid content resulted in a high methanol concentration for a given pulping condition using the same wood simply due to the dilution of the sample. Therefore, it will be appropriate to normalize the methanol concentration in weak black liquor by the solid content to present the data in the future.

*VOC liquid content measurements in various mill streams*

The liquid methanol contents in various Kraft mill streams from Mill C were also conducted using the present method, the results are shown in Table II. Mill C is a nonbleached Kraft paper mill. For this particular mill the data indicate: (1) the weak wash stream in the recovery cycle does not contain methanol, (2) the shower water and filtrate streams in the washers contains a significant concentration of methanol, (3) the condensated blow tank steam from the digester also has a high content of methanol as indicated by the measurement of the sample from the hot water tank, (4) the white water from the paper machine head tank for the present nonbleached mill contains some methanol, and (5) weak black liquor has a significant content of methanol. The measured methanol contents in various streams are reasonable with practical knowledge.

## SUMMARY

A new method using headspace gas chromatography for determination of VOC content in mill streams has been developed. The method is based on vapor-liquid phase equilibrium of the species to be determined. It has the advantages of being rapid, automated, and accurate

also no calibration is required. It can be universally applied to any mill stream samples or other industrial and environmental streams.

The present method has been validated with three VOC-water solutions of known concentrations (methanol-water, MEK-water, acetone-water). The comparisons of the measured VOC concentrations in the three solutions in a combined concentration range over three orders of magnitude with the known concentrations are excellent. The measured liquid methanol content in Kraft mill liquors with the present method also showed a good agreement with the data obtained by the NCASI method.

Preliminary measurements of VOC contents in various mills streams were conducted. More measurements are needed in the future to obtain conclusive results.

## ACKNOWLEDGEMENTS

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## REFERENCES


1. Venketesh, V., Lapp, W., and Parr, J., "Millwide methanol balances: Predicting and evaluation HAPs emissions by utilizing process simulation techniques," *1996 TAPPI International Environmental Conference and Exhibits* 31 (1996).
2. Jain, A., "Impact of water system closure on HAP and VOC emission from process vents," *TAPPI Minimum Effluent Mills Symposium* (1996).
3. Gunshefki, M. and Cloutier, S., "NCASI Procedures for collection and analysis of black liquor samples," *NCASI Technical Memo* (1994).
4. Ioffe, B.V. and Vitenbery, A.G., "Head-Space Analysis and Related Methods in Gas Chromatography," John Wiley & Sons, Inc., New York, (1984).
5. Hussam, A. and Carr, P.W., "Rapid and precision method for the measurement of vapor/liquid equilibria by headspace gas chromatography," *Anal. Chem.* 57:793 (1985).
6. Kolb, B., Welter, C. and Bichler, C., "Determination of partition coefficient by automatic equilibrium headspace gas chromatography by vapor phase calibration," *Chromatographia* 34:235 (1992).
7. Hewlett, P., "Analysis of Organic Impurities in a Recycled Paper Product Using HP7694 Headspace Automatic Sampler," Hewlett Packard Corp., (1993).
8. Bauer, H.H., Christian, G.D. and O'Reilly, J.E., "Instrumental Analysis," Allyn and Bacon, Inc., Boston, (1978).
9. Stratton, R.N. and Zhu, J.Y., "Measurement of liquid methanol content in black liquors," Institute of Paper Science and Technology, Technical Paper Series No: 619 (1996).

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Fig. 3. Comparison between the measured and the known VOC concentrations in standard VOC-water solutions.

Fig. 4. A typical chromatogram of a hardwood Kraft black liquor vapor obtained from headspace GC analysis.

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Table I. Comparisons of measured methanol concentration in four black liquors using the NCASI method and the present method.

Table II. Methanol concentration in various mill streams measured using the present method.

## Nomenclature

| | |
|---|---|
| $P$ | vapor partial pressure of the solute |
| $H$ | dimensional Henry's constant |
| $C$ | liquid concentration of the solute |
| $n$ | vapor moles of the solute |
| $A$ | measured GC peak area |
| $V$ | volume |
| $V_t$ | total volume of the sample vial |
| $V_{loop}$ | volume of the sample loop |
| $a$ | correction factor for sample solution at the temperature, $T$ |
| $K$ | a constant response factor |
| $R$ | gas constant |
| $T$ | temperature in the headspace |

Subscript and superscript

| | |
|---|---|
| $0$ | the initial state of the sample before put into the sample vial |
| $1$ | the equilibrium state within the sample vial before standard addition |
| $2$ | the equilibrium state within the sample vial after standard addition |
| $g$ | vapor phase |
| $l$ | liquid phase |
| $s$ | the state of the concentrated liquid solution used for standard addition |

Table I. Comparisons of measured methanol concentration in four black liquors using the NCASI method and the present method

| SAMPLE | Solid Content (%) | Methanol Concentration (ppm) | | |
|---|---|---|---|---|
| | | NCASI method | Present method | Difference (%) |
| Softwood, Mill A | 15.2 | 775 | 736 | 5.0 |
| Hardwood, Mill A | 17.1 | 961 | 906 | 5.7 |
| Softwood, Mill B | 11.5 | 434 | 419 | 3.5 |
| Hardwood, Mill B | 10.8 | 527 | 560 | -6.3 |

Table II. Methanol concentration in various mill streams measured using the present method

| Sample Number | Sample Description | Methanol Concentration (ppm) |
|---|---|---|
| 1 | weak wash liquor from recovery cycle | 1 |
| 2 | white water from paper machine head tank | 40 |
| 3 | pulp wash shower water first stage digester (D1) | 277 |
| 4 | filtrated stream from first washing stage (D1) | 251 |
| 5 | filtrated stream from second washing stage (D1) | 238 |
| 6 | filtrated stream from first washing stage (D2) | 172 |
| 7 | filtrated stream from second washing stage (D2) | 201 |
| 8 | condensated stream of blow tank steam in hot water tank | 315 |
| 9 | weak black liquor to evaporator | 272 |

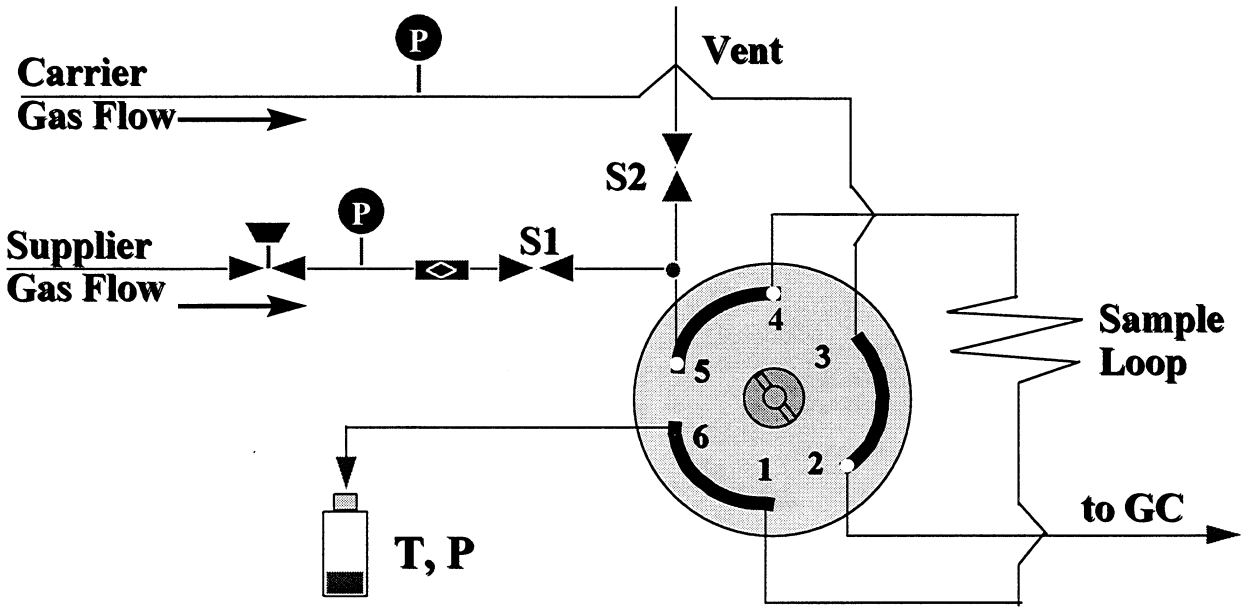
Carrier
Gas Flow
P
Vent
S2
Supplier
Gas Flow
P
S1
4
3
5
6
1
2
Sample
Loop
to GC
T, P

Fig. 1

Signal (peak area)
40
50
60
70
0
10
20
30
40
70°C
Equilibrium time, min.

Fig. 2

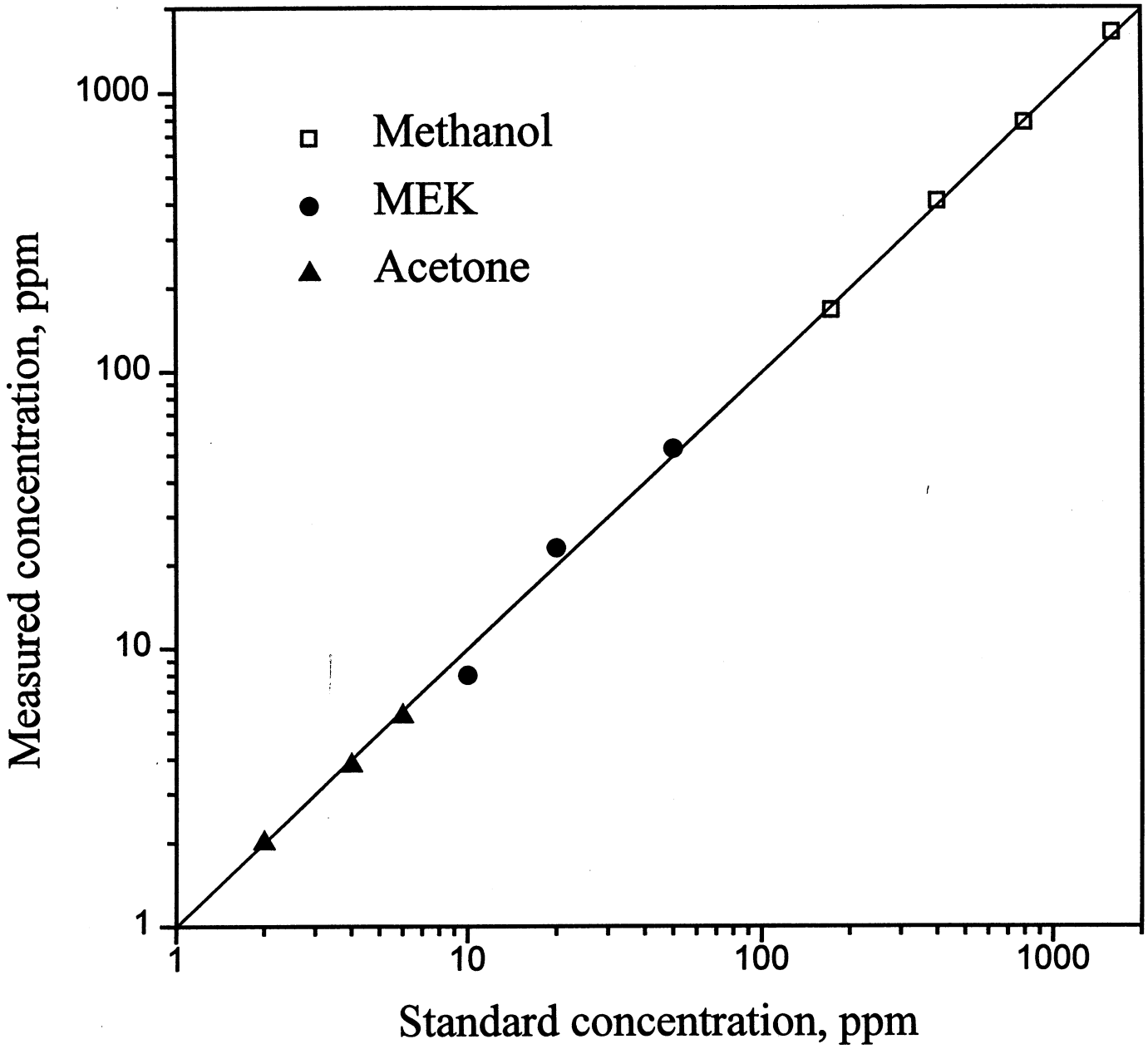
Methanol
MEK
Acetone
Measured concentration, ppm
Standard concentration, ppm
1
10
100
1000
1
10
100
1000

Fig. 3

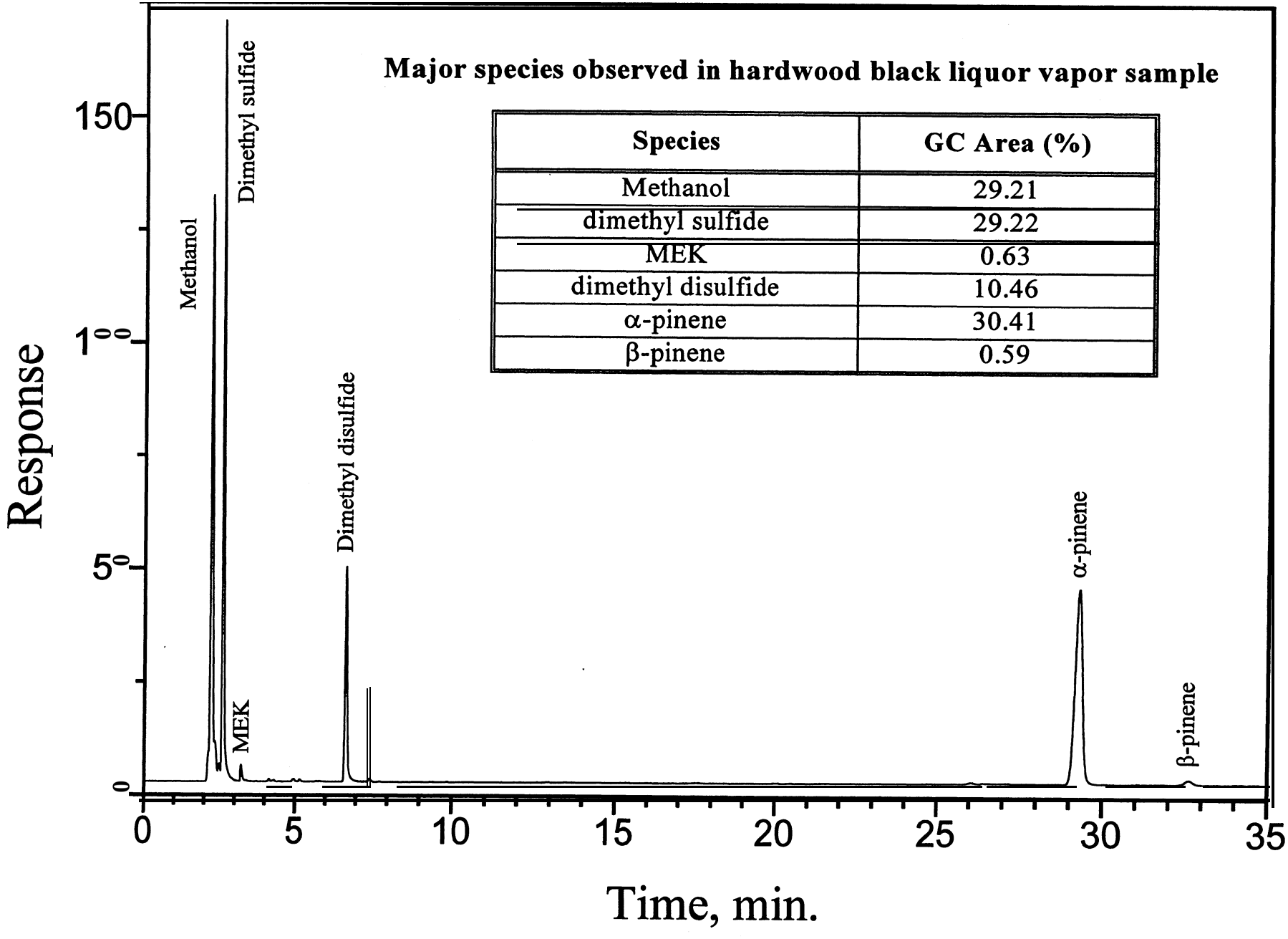
Major species observed in hardwood black liquor vapor sample
Species | GC Area (%)
Methanol | 29.21
dimethyl sulfide | 29.22
MEK | 0.63
dimethyl disulfide | 10.46
α-pinene | 30.41
β-pinene | 0.59
Methanol
Dimethyl sulfide
MEK
Dimethyl disulfide
α-pinene
β-pinene
Response
Time, min.
0
50
100
150
0
5
10
15
20
25
30
35

Fig. 4